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(54) Synthetic resin film with activated surface and process for activating same

(57) A seamless tubular synthetic resin film for wrapping meat is a single or multi-layered film in which the single layer or the inner most layer is made from an olefin or vinylidene chloride resin having substantially no functional groups, such as acid or acid amide radicals. The inner surface of the tube is activated so that after treatment with an aqueous solution of albumin and starch, from 1.1 to 2.2 milligrams of albumin and starch adhere to the activated surface and the haze of the treated surface is not less than 75%. The inner surface of a tubular film is activated by passing the film 1, between spaced electrodes 4, 4', with the outer surfaces of the film in contact with the electrodes and causing a corona or glow discharge between the inner surfaces in the presence of a gas, *eg* air. One surface of a *flat film* can be activated in a similar manner by folding the film into a two layer form with the one surface on the inside.

FIG. 4

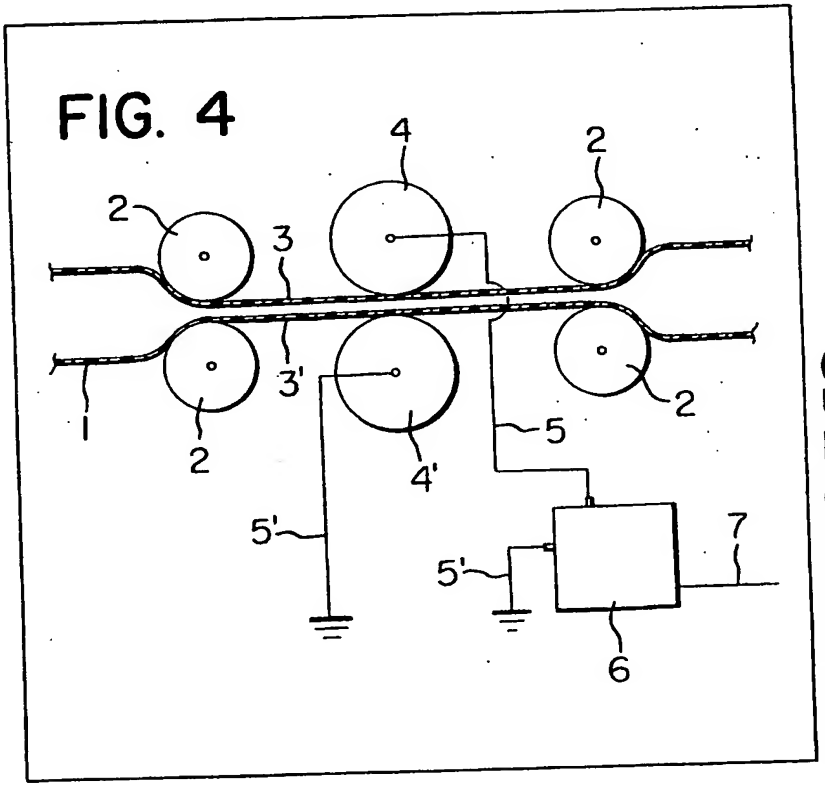

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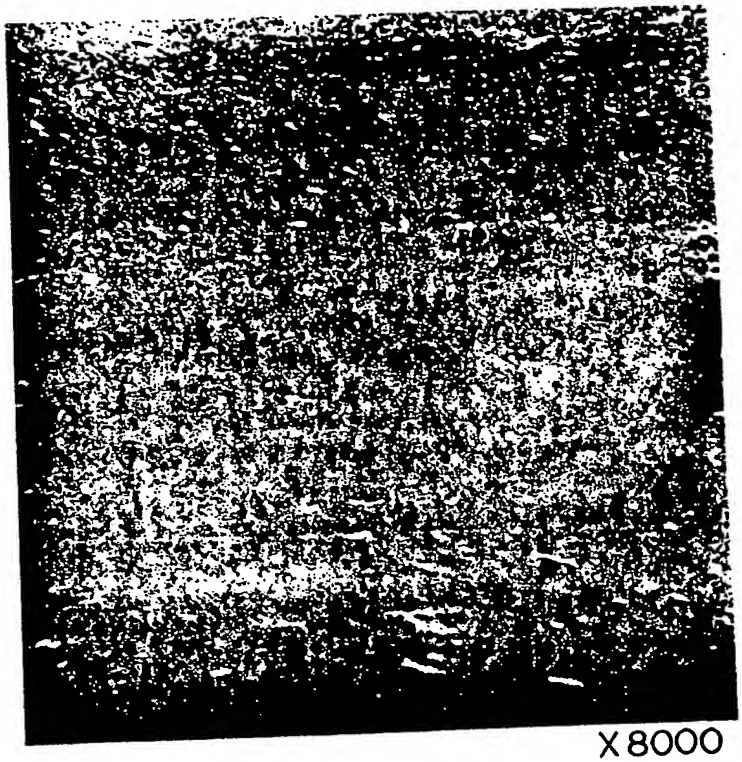
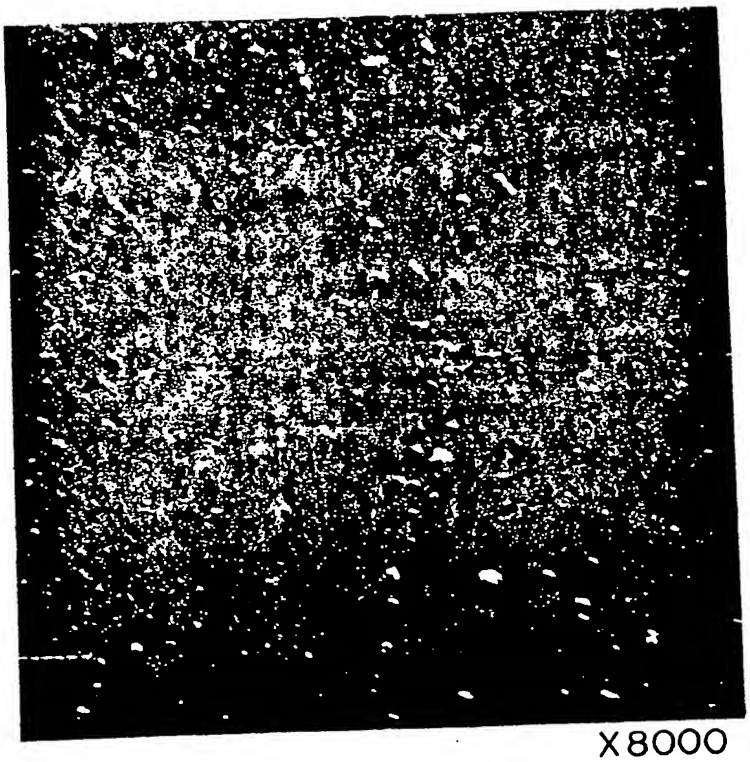
FIG. 1



X8000

FIG. 2



X8000

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FIG. 3

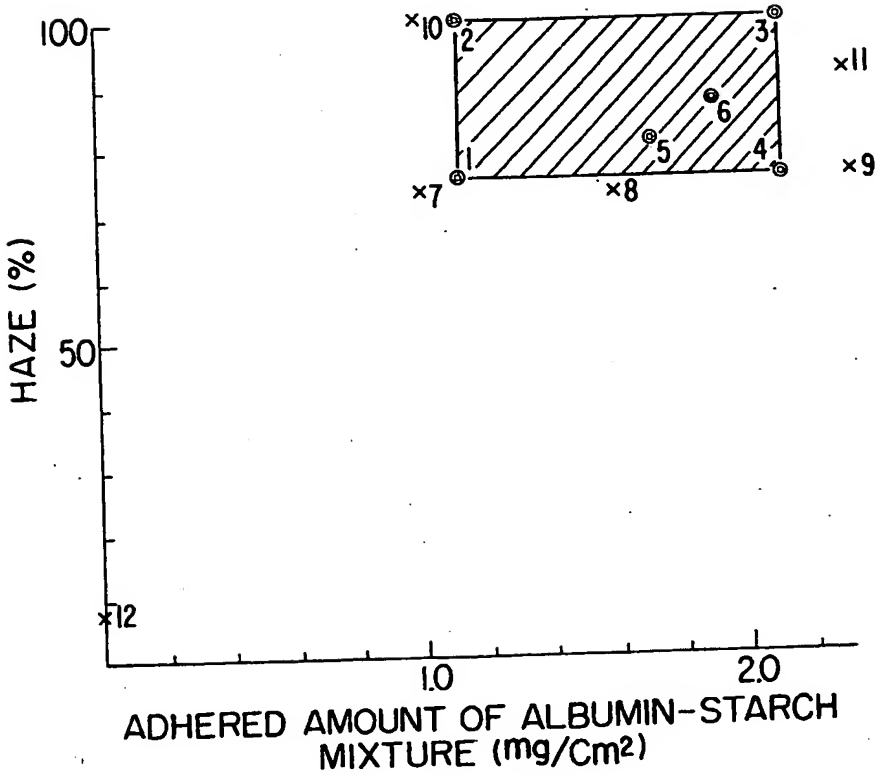

FIG. 4

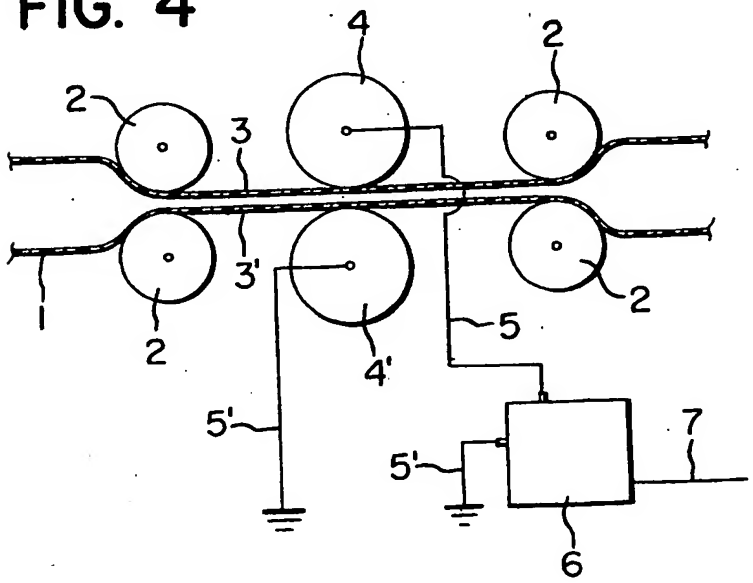

FIG. 5

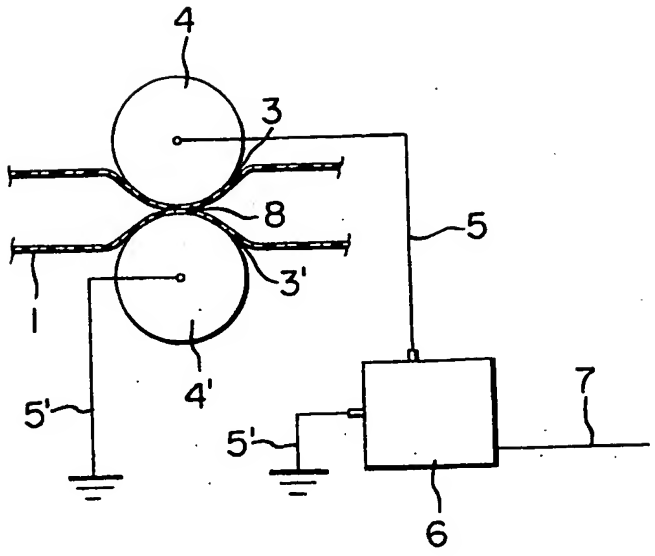

FIG. 6

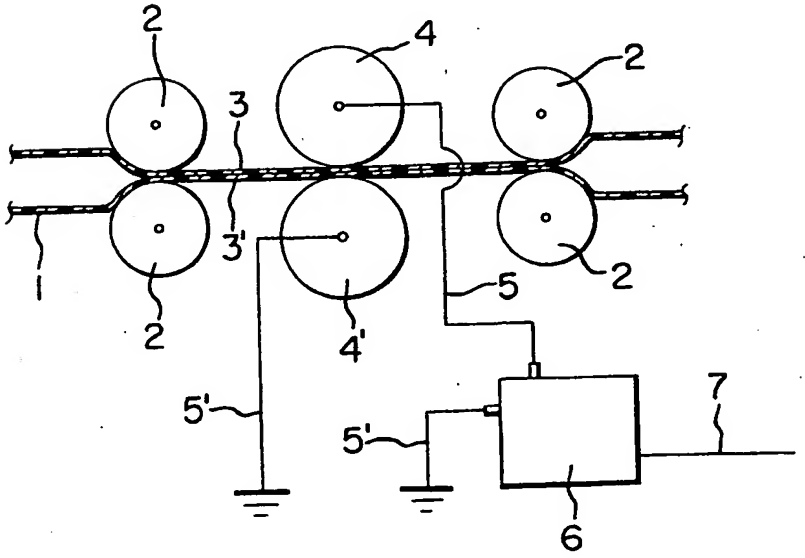

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FIG. 7

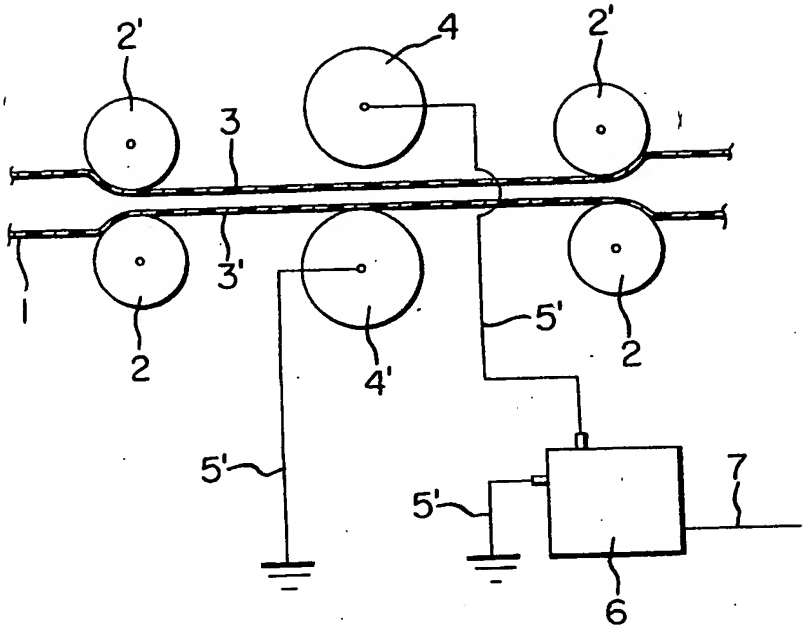
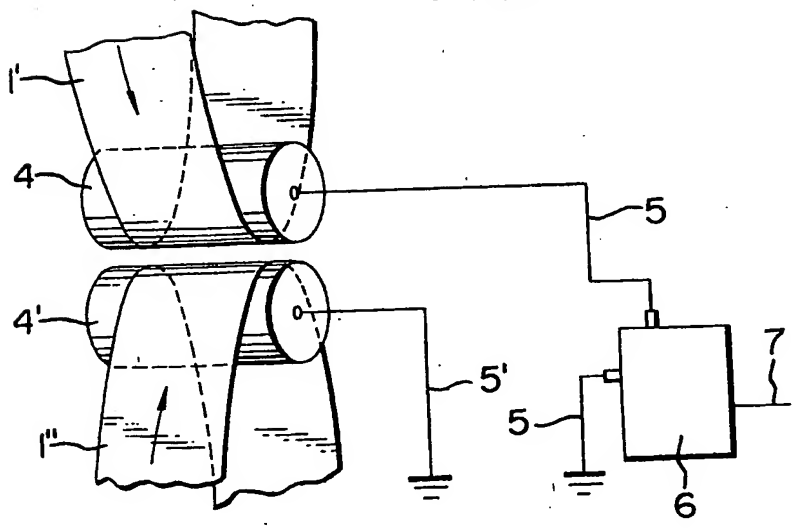


FIG. 8



SPECIFICATION

Synthetic Resin Film with Activated Surface and Process for Activating the Same

Background of the Invention

It is well known that synthetic resin films have been treated for the activation of their surfaces. It is further known that the thus treated films exhibit better printability and higher levels of adhesion to meaty substances (meat-adhesiveness) than their corresponding untreated films.

It is also known that when a film made of a resin of a high barrier property such as, for example, vinylidene chloride resin is treated for the activation of its surface and the resultant treated film is used for shrink packaging a meaty substance, the film is brought into tight contact with the meaty substance because of its high capacity for shrinkage, the surface of the film and that of the meaty substance come into intimate union because of the film's high adhesiveness to meaty substance, and the finished package provides a notably improved storageability for the meaty substance because of the film's barrier property.

The conventional films with activated surfaces, however, hardly meet the qualitative needs of the market because of varying disadvantages such as, for example, insufficiency of the activity assumed in consequence of the surface treatment, deficiency of the meat-adhesiveness in spite of satisfactory printability, susceptibility of the meat-adhesiveness to possible variation in the quality of meaty substance subjected to packaging, degradation of the barrier property due to occurrence of pinholes or other similar defects, lack of uniform distribution of the activity to film surface and consequent lack of uniform distribution of printability and meat-adhesiveness in the film, and heavy dispersion of the degree of imparted activity between films taken from different lots as well as films taken from different parts of one and the same lot.

A possible cause for all these adverse phenomena may be the fact that it is difficult for the surface of a given film to be uniformly activated to an extent of assuming a required level of activity.

Specific difficulties encountered by different pieces of the prior art will be cited herein below.

(1) The film which is produced by forming in the inner surface of a tubular film a layer of vinylidene chloride resin latex containing an acrylic acid radical, etc. as disclosed in Japanese Patent Publication No. 35947/1975 involves disadvantages including heavy qualitative change both within and between lots, high susceptibility of the meat-adhesiveness to the change in the quality of meaty substance given to be packaged, and deficiency in productivity and ease of opening during the packaging operation. Since these disadvantages are intrinsic problems of the technique of manufacture itself, they have no room for any further improvement. Specifically, this process comprises disposing inside a tubular film a reservoir for the aqueous solution of a resin latex possessing active power, applying the resin latex to the inner surface of the tubular film by squeezing the opposite ends of the reservoir with pinch rollers and allowing the applied layer of resin latex to be set and dried into a film by the heat of stretching. By this method, however, the latex film cannot be uniformly formed and the concentration of the resin latex in the reservoir falls in a short time (of the order of scores of minutes) so much as to cause quality dispersion in the direction of time passage. Prevention of this trouble requires an extra step of cutting the film after fixed intervals of time and inserting the remaining untreated film around another reservoir. This extra step inevitably entails a time-course change in the amount of resin latex adhered to the inner surface of tubular film and degrades the yield of the overall operation of the process. There is further involved a phenomenon that the ease of opening of the tubular film is impaired because of insufficiently uniform drying of the applied film of resin latex.

(2) The film which is formed by incorporating a surface layer made of a multi-component polymer containing an acrylic acid radical, an acid amide radical, etc. as disclosed in French Patent Disclosure No. 1,503,246 turns out to be a product deficient in meat-adhesiveness and ability to permit long preservation of meaty-substances. The cause for the disadvantage is that, owing to the deficient film-forming property of the multi-component polymer containing the acrylic acid radical, etc., the film assumes an uneven wall thickness, suffers from heavy occurrence of pinholes and fails to retain sufficiently and put to best advantage the gas barrier property of the basal resin itself. If the contents of the acrylic acid radical, etc. in the polymer are lowered with a view to precluding such drawbacks, the distribution of the acrylic acid radical, etc. within the film becomes uneven to the extent of preventing the film from fully manifesting its meat-adhesiveness.

(3) The process disclosed in Japanese Utility Model Laid-open Publication No. 47578/1977 and Japanese Patent Laid-open Publication No. 18770/1976 involves subjecting the surface of a given film to electric discharge (or plasma). The film thus produced is folded and welded with the treated surface on the inside to give rise to tubular film. Although this film exhibits an improved meat-adhesiveness compared with its corresponding untreated film, the adhesion of meaty substance to the film surface occurs unevenly (in the form of spaced stripes), possibly indicating that the required active power is not uniformly distributed in the film surface. Further, this process cannot produce a tubular film unless there is performed an additional operation of cutting the produced film into strips of a fixed width, folding each strip and welding joined edges. In this respect, this process can be clearly distinguished from the present invention in terms of technical level.

(4) The official gazette of Japanese Patent Publication No. 6157/1968 may be cited as a piece of

literature which discloses a process capable of activating the inner and outer surfaces of a seamless tubular film by subjecting the film to corona discharge. The inventors, on evaluating this process by faithfully following the procedure disclosed, have ascertained that the outer surface of the tubular film shows a definite sign of improved printability, whereas the inner surface thereof hardly shows any appreciable sign of improvement in printability. The test of this film for meat-adhesiveness has shown that the outer surface side of the film exhibits the property unevenly (in the form of spaced stripes) and the inner surface side thereof does not exhibit the property at all. This disadvantage may possibly be ascribed to the fact that the expression "activation" allows for variations in the manner of activation and the degree of activation and the degree of activation satisfying the meat-adhesiveness contemplated by the present invention is such that it can hardly be accomplished by the mere degree simply permitting improvement in the printability.

The inventors performed a study on the activation of film surface in research of a breakthrough to the various difficulties encountered and consequently ascertained that when two strips of film arranged to be slid on a pair of roller electrodes 4, 4' are advanced in the directions indicated by the arrows while the electrodes 4, 4' are separated by a varying distance and are kept under continued application of a high voltage as illustrated in Fig. 8 of the drawing attached hereto, there occurs electric discharge between the opposed surfaces of the two strips of film to cause in the film a phenomenon of activation different from the activation heretofore attained by the prior art. They subsequently developed effective means for determining the degree of activation and the uniformity of activation and continued a further study and, consequently, succeeded in improving the principle of the process of treatment described above so as to be adaptable for treatment of tubular film. Thus, the present invention has been accomplished.

Summary of the Invention

It is therefore, the primary object of this invention to provide a novel film wherein a high level of active power is uniformly imparted to one surface of the film so as to give to the film not merely effective printability but also a meat-adhesiveness capable of withstanding qualitative change in the meaty substance as well as effective printability without impairing the barrier property and other properties possessed intrinsically by the resin of which the film is made.

Another object of the present invention is to provide a tubular film wherein the aforementioned state of activation is materialized in the inner surface of the tubular film.

A further object of the present invention is to provide a packaging film for use with meaty substances, which film permits the meaty substances to be stored intact for a notably long period never attainable with any of the conventional activated films.

Specifically, this invention relates to a single- or multi-layered seamless tubular synthetic resin film wherein when single-layered said tubular film is made of either an olefin resin or a vinylidene chloride resin containing substantially no functional group such as acid radical or acid amide radical and wherein when said tubular film is multi-layered the inner surface layer of said film is made of either an olefin resin or a vinylidene chloride resin containing substantially no functional group such as acid radical or acid amide radical, characterized in that the inner surface of said tubular film is activated to such an extent that the quantity of a mixture adhered to said inner surface ranges from 1.1 to 2.2 milligrams per square centimeter, said mixture consisting of albumin and starch and that the haze of said film to which the mixture adheres is not less than 75%, when said surface is treated with a mixture consisting of an aqueous albumin solution and starch and further to a process for treating a tubular or flat synthetic resin film consisting of at least one layer with an electrode assembly comprising at least a pair of electrodes which are spaced and opposed to each other and which a high voltage current is applied to, characterized by activating inner film surface not in contact with said electrodes by means of conducting corona or glow discharge in the presence of a gas between inner film surfaces spaced and opposed to each other, while travelling said tubular film or flat film of double ply in the state of keeping the outer surface of said tubular film or the outer surface of each ply of said flat film in contact with said electrodes.

Now, the present invention will be described in detail with reference to the accompanying drawing.

Brief Explanation of the Drawing

Fig. 1 and Fig. 2 are photographs showing the inner surfaces of the treated tubular film of the present invention and the untreated tubular film respectively enlarged to 8,000 magnifications with a microscope. Fig. 3 is a graph showing the results of Table 2. Fig. 4 and Fig. 5 are sectional explanatory diagrams each illustrating a process for electric discharge treatment convenient for performing the treatment of the present invention. Fig. 6 and Fig. 7 are sectional explanatory diagrams each illustrating a comparative process for electric discharge treatment. Fig. 8 is a diagram illustrating the principle of the process of treatment involved in the present invention.

Detailed Description of the Invention

The most important requirements that are to be satisfied by the film to which the present invention is directed are:

A) That the activated resin layer should be formed of a polyolefin resin or a vinylidene chloride resin containing substantially no functional group such as an acid radical or an acid amide radical.

B) That the surface of the resin layer mentioned above should be activated to conditions falling in the range enclosed with a solid line as illustrated in Fig. 3.

It is imperative that these two requirements should be satisfied at the same time.

Fig. 3 represents a graph showing the limits to the activity effected in the surface of the film according to the present invention. In the graph, the values obtained of the film of this invention (those indicated by double circles "◎" in Table 2) and the values obtained of the film not conforming with this invention (those indicated by crosses "x" in Table 2) are clearly distinguished from each other. More specifically, this graph shows that when a mixture consisting of the aqueous solution of albumin and starch at a specific ratio to be described hereinafter is applied to the activated surface of the film of this invention, the amount of the mixture adhered to the surface falls in the range of from 1.1 to 2.2 mg/cm² and the haze of the film due to the adhesion of the mixture is not less than 75%.

This method for the evaluation of activation is characterized by being three-dimensional in the sense that even when the amount of the mixture adhered to the film surface is large, for example, the haze of the film does not have a sufficiently high value if the adhesion occurs unevenly (in the form of spaced stripes) or even when the adhesion of the mixture to the film surface is even, the haze falls to have a high value if the amount of the mixture adhered to the film surface does not exceed a certain level.

The requirement A) indicates that the present invention is not directed to polyamide films, polyester films and other films which assume high levels of activity without requiring any special treatment for activation. This distinction becomes all the more clear from the appreciation of the fact that this invention is based on a unique principle entirely different from the principle of the prior art which accomplishes the activation of the film surface by either applying to the film surface a functional group such as an acid radical or acid amide radical or exposing the film surface to such a functional group and that the present invention consequently precludes successfully all the drawbacks suffered by the prior art. The word "substantially" as used in this requirement, therefore, embraces a meaning that the absence of the functional group is to such an extent as to enable the film to acquire the meat-adhesiveness aimed at by this invention. In short, this invention is perfectly accomplished without any recourse to the acid radical and other functional groups which tend to impair the film quality and the producibility of the film.

The requirement B), on the other hand, indicates that when the amount of the mixture adhered to the film surface is smaller than the lower limit 1.1 mg/cm² of the stated range, the film exhibits printability of a level generally passable but hardly satisfactory from the standard contemplated by the present invention and the film, if the printability may be satisfactory from the practical point of view, fails to assume passable meat-adhesiveness. At times, such a film may exhibit satisfactory adhesiveness to fish meat but fails to show any appreciable adhesiveness to livestock meat. In this film, the meat-adhesiveness is quite susceptible to the qualitative change in meaty substances being packaged with the film. Conversely when the amount of the mixture adhered to the film surface is greater than the upper limit 2.2 mg/cm² of the range, the film exhibits lower barrier property than is acceptable and suffers from occurrence of pinholes. In this sense, the upper limit 2.2 mg/cm² is a fairly conservative value.

Even when the amount of the aforementioned mixture adhered to the surface of the film falls in the stated range of from 1.1 to 2.2 mg/cm², the condition of the adhesion of meat to the film in the finished package is ununiform if the haze of the film due to the adhesion of meat is smaller than 75%. Even when the amount of the meat adhered to the film is large, the film's ability to preserve the meaty substance intact for a long period is not obtained. Consequently, the film suffers from a disadvantage that the film's preservability of meaty substance becomes susceptible to the qualitative change of meaty substance being packaged.

Through experiments, the inventors have ascertained that the haze of a given film does not necessarily increase with the increasing amount of meaty substance adhered to the surface of the film and that the amount of meaty substance adhered does not necessarily increase when the haze of the film increases.

The haze of a given film can be increased by incorporating a pigment or some other suitable additive in the resin as the basal material for the film. Even if the haze is increased in this film by such incorporation of an additive, the amount of meaty substance adhered to the film is not increased at all. The data of Fig. 3 are those obtained of film samples invariably in a colorless state. Incorporation of a pigment or some other similar additive to the film does not affect the ranges of numerical data specified for the present invention.

Supplementary requirements to be fulfilled by the film of this invention are that the film should incorporate at least in the surface thereof a layer of vinylidene chloride resin and that the surface of the film is activated. It is important that these requirements are satisfied at the same time. For the activation of the surface of the film, an electrical treatment may be cited as an effective measure capable of activating a material which is intrinsically devoid of activating property.

The activation required to be effected on the film or seamless tubular film contemplated by the

present invention can bring about an equal effect no matter whether the film is formed of a single layer or a plurality of layers (including combinations of layers of same or different resins). To ensure improvement in the film's ability to preserve meaty substances intact for a long time, it is desirable to use in the film construction a layer of vinylidene chloride resin excelling in gas barrier property and abounding with flexibility or, where permissible, to use the layer of vinylidene chloride resin in the surface side of the film exposed to intimate contact with the meaty substance being packaged with the film.

The electrical treatment as an effective measure for the activation means a phenomenon such as corona discharge or glow discharge which, on application to the film, impart active power to the film. It is, therefore, entirely dissimilar to the kind of treatment which enables a highly active substance to be deposited inside the film or which activates the inner surface of the film by exposing the surface to such an active substance. This distinction between the activation by the present invention and the activation by the prior art is self-evident from the comparison of the respectively produced films and their surface layers. It is further endorsed by the many outstanding advantages issuing from the fact that this invention, owing to the activation, permits a long strip of film free from qualitative ununiformity can be continuously produced in the form of a seamless tubular film.

Moreover from the electrical treatment of the present invention, there is derived an amazing advantage that only the inner surface of the tubular film is selectively activated. In the present invention, this advantage never attained by the prior art constitutes itself a salient feature in the sense that, owing to this particular advantage, the present invention permits a very long strip of film to be easily produced in the fom of a seamless tubular film and enables the activation of the film to be effected to an outstanding level as compared with the tubular film obtained by the steps of subjecting the surface of a sheet film to an electrical treatment, folding the treated film with the treated surface on the inside and welding the joined edges of the film according to the prior art.

The inventors have studied the difference the activation by the present invention and that by the prior art from various angles. Specimens of tubular films treated and not treated as contemplated by the present invention were photographed in 8,000 magnifications each with a micrograph. The photomicrographs thus obtained will be compared for the determination of the difference. Comparison of Fig. 1 (photomicrograph of the specimen of this invention) with Fig. 2 (photomicrograph of the specimen of untreated film) does not lead one to a conclusion that the surface of the film of Fig. 1 is coarser than that of Fig. 2. The comparison leads to a possible conclusion that the microscopic appearance of the surface of the film of the present invention differs from that of the film assuming a peculiar surface appearance claimed to result from the corona discharge treatment performed in accordance with the prior art.

From the foregoing comparison, it is found that the product of this invention is not a mere improved version of the product of the prior art, the improvement comprising enhanced effects such as, for example, an increase in the amount of meaty substance adhered to the film surface and an addition to the strength of adhesion of meaty substance to the film surface. In the evaluation of the meat-adhesiveness expressed in terms of the amount of meaty substance adhered to the film surface, for example, the meaty substance adheres in a thick layer unevenly (in the form of spaced stripes) to the film of the prior art, whereas it adheres uniformly (with virtually no bare surface) to the entire surface of the treated area of the film of the present invention. Besides, the product of this invention possesses meat-adhesiveness highly stable to possible qualitative change (such as in oil content) of meaty substance. Thus, the product of this invention exhibits effects different from those of the product of the prior art. Further, the meat-adhesiveness of the film varies very little between films taken from different portions of one same lot or between films from different lots. The barrier property intrinsically possessed by the film itself is retained in its unimpaired state. The film enjoys an additional advantage that it does not permit any appreciable occurrence of pinholes.

The comprehensive analysis of the various effects brought about by this invention as described above has led to successful selection of the range of Fig. 3 which serves as an effective criterion for distinguishing the product of this invention from products of the prior art.

In the graph of Fig. 3, the vertical axis is graduated by the scale of haze (in %) and the horizontal axis by the scale of the amount of the mixture of albumin and starch (in mg/cm^2) to be specified herein below.

The methods for rating the meat-adhesiveness and the haze of a given film by use of the aforementioned mixture consisting of the aqueous solution of albumin and starch at a specified ratio have been developed and further improved for perfection by the inventors. These methods are defined below.

Method of Rating

Methods for rating the meat-adhesiveness and haze of film by use of mixture of aqueous solution of albumin and starch.

A) Preparation of Specimen

The mixture is prepared by thoroughly stirring 100 parts by weight of an aqueous 25% egg

albumin (Grade 1, according to JIS K8068) with 100 parts by weight of starch (flour of Grade 1, made by Nisshin Mill).

From a given sample of a long strip of seamless tubular film, 10 tubular specimens each having the same flat width as the sample and a length of at least 100 mm are collected. Each film tube, with one cut end tied, is filled to capacity with the mixture of albumin and starch prepared as described above in such a way that no air is introduced with the mixture. Then the film tube is tied on the remaining cut end to produce a cylindrical package. The package is immersed in hot water at 90°C for 30 minutes. At the end of the standing in the hot water, it is removed, then cooled in a current of cooling water at 20°C for one hour, dried on a filter paper to remove water drops adhering to the package surface and then left to stand in a room kept at 20°C±1°C and RH 60%±5% for three hours.

At the end of the standing in the room, two circumferential cuts are inserted at a longitudinal interval of 50 mm at a randomly selected portion around the middle of the entire length of the cylinder and then a longitudinal cut is inserted across the zone enclosed with the aforementioned two circumferential cuts to have the resultant annular segment of film 50 mm in width ripped off the surface of the cylinder. The rectangular piece of film thus obtained is used as a specimen. (A total of ten such specimens are obtained).

B) Measurement of Amount of Mixture Adhered to the Specimen (in mg/cm²)

Five specimens are selected from the total of ten and each of the five specimens is accurately weighed (W_1). This weighing must be carried out in a room kept at 20°C±1°C and RH 60%±5% within five minutes from the time the specimen is ripped off the cylinder. After the weighing, the mixture of albumin and starch adhering to the surface of the specimen is quickly removed in running water, and the remaining film is dried on a filter paper to remove water drops adhering to the film surface. The film is then dried in a room at 20°C±1°C and RH 60%±5% for three hours. Then the dried film is accurately weighed (W_2).

Formula for calculation:

$$\text{Amount of mixture (mg/cm}^2\text{)} = \frac{W_1 - W_2}{\text{Area of specimen}}$$

The amount of the mixture adhered to the film is to be determined by obtaining the value of the formula with respect to each of the five specimens and calculating the arithmetic mean of the five values.

C) Haze (in %)

Each of the remaining five specimens is stretched out and the central portion about 25 mm in diameter which is consequently held taut is tested for haze (in %) by the method of ASTM D1003—16. This test must be carried out in a room at 20°C±1°C and RH 60%±5% within 30 minutes from the time the specimen is prepared. The haze is to be determined by obtaining this value of haze with respect to each of the five specimens and calculating the arithmetic mean of the five values.

Now, the process of this invention by which the film of the invention is manufactured will be described in detail with reference to the accompanying drawing.

Fig. 8 is a diagram illustrating the principle of the process of treatment according to the present invention.

With reference to Fig. 8, the process of this invention comprises causing a pair of sheet films 1', 1'' of synthetic resin to be slid on a pair of roller electrodes 4, 4'. In this case, the roller electrodes 4, 4' are so disposed that the inner surfaces of the films 1', 1'' are opposed to each other across a space filled with a gas and the outer surfaces of the films 1', 1'' are held in intimate contact with the surfaces of the roller electrodes 4, 4' kept under continued application of a high voltage. In this manner, the films are longitudinally advanced at an equal speed. The incoming power from an electric power source 7 is converted into a high voltage by means of a high-voltage generation unit 6 and the resultant high-voltage power is fed via a conductor 5 to the electrode 4. Denoted by the numeral 5' is a grounding cable. In the device of this diagram, when the gap separating the films 1', 1'' on the roller electrodes is adjusted to a proper value, there occurs electric discharge between the films 1', 1'' and notable activation is caused consequently on the opposed surfaces of the films 1', 1''.

Fig. 4 and Fig. 5 are sectional explanatory diagrams each illustrating a typical process for electric-discharge treatment convenient for performing the treatment of this invention. Fig. 6 and Fig. 7 are sectional explanatory diagrams each illustrating a device used for performing a comparative electric-discharge treatment.

In the device of Fig. 4, a tubular film 1 of synthetic resin filled with a gas and kept in motion is depressed by rolls 2 into a flatly collapsed form. In this case, the flattening of the tubular film is made to such an extent that the two major parallel portions of the inner surface of the tubular film are not brought into intimate contact with each other but are opposed to each other across a gap permitting a gas to exist within the tubular film. In this case, the gap is desired to be as uniform as possible throughout the entire width of the partially collapsed tubular film. The corresponding major parallel outer surfaces 3, 3' of the tubular film so flattened and kept in motion are held in intimate contact with

the pair of electrodes 4, 4' kept under continued application of a high voltage so as to induce the phenomenon of corona discharge or glow discharge (not shown) between the opposed inner surfaces of the film and consequently give rise to the phenomenon of activation in the inner surface of the tubular film. In the application of the high voltage, the question as to which of the electrodes 4, 4' is used as a positive pole or negative pole is not critical. In the device of the construction of Fig. 4, the incoming electric power from the electric power source 7 may be converted by a high-voltage generation unit 6 into a high-voltage power and the resulting power fed via the conductor 5 to the electrode 4. The numeral 5' denotes a grounding cable.

Fig. 5 represents a typical way of partially collapsing the tubular film as involved in the present invention. A part of the tubular film of synthetic resin filled with a gas and kept in motion is pushed toward each other and consequently flattened by means of a pair of electrodes 4, 4' kept under continued application of a high voltage. In this case, the flattening of the tubular film is made in such a manner that the two parallel portions of the tubular film come into tight contact with each other at the contact point 8 of the electrodes 4, 4' and, on either side of this contact point 8, they are opposed to each other across a gap. Since the portions of the film thus opposed to each other on either side of the contact point have their respective outer surfaces held in contact with the electrodes kept under continued application of a high voltage, there can be generated the phenomenon of electric discharge between the corresponding inner surfaces of the film.

The most important requirements to satisfy the process of the present invention are consisting of (a) travelling the tubular film or flat film of double ply between at least a pair of electrodes in the state of keeping the outer surface of the tubular film or the outer surface of each ply of the flat film in contact with said electrode, (b) conducting corona or glow discharge in the presence of a gas between film surfaces spaced and opposed to each other and (c) thereby activating the inner film surface which is not in contact with the electrode.

The objects of the present invention cannot be accomplished unless the above three requirements (a), (b) and (c) are simultaneously satisfied.

The device illustrated in Fig. 6 is a variation of the device of Fig. 4 in that the rolls 2 are brought toward each other so much that the two major parallel portions of the inner surface of the tubular film come into intimate contact with each other and the corresponding major parallel portions of the outer surface of film are held in tight contact with the pair of electrodes kept under continued application of a high voltage. In this varied device, no appreciable increase can be expected in the active power in the inner surface of the film.

The device illustrated in Fig. 7 is a variation of the device of Fig. 4 in that one of the pair of electrodes is disposed so as not to remain in contact with the film surface. Neither in this varied device can there be expected any appreciable increase in the active power in the inner surface of the film.

Any gas can effectively be used to fill the gap between the opposed inner surfaces of the tubular film or the flat film of double ply. Examples of such gases include air, nitrogen, helium and argon. This is possibly because the activation contemplated by the present invention, unlike the activation involved in the prior art, is not required to produce an oxidized film on the film surface or to coarsen the film surface.

In this treatment, the gap between the inner surfaces is variable with the magnitude of the electric power used for the treatment and other conditions of the treatment. When the gap is greater than 8 mm, the active power imparted to the film is too small to make the treatment economical. It is, therefore, desirable that the gap should be limited to within 5 mm and should not be varied as much as possible for the purpose of imparting uniform active power to the film.

It is advantageous for the purpose of the treatment to keep the surface temperature of the film during the electric discharge from falling below the secondary transition point of the film. In this case, since the electric-discharge treatment is generally carried out continuously on a long strip of film kept in motion, this electric-discharge treatment cannot be expected to elevate the surface temperature of the film. For the electric-discharge treatment to be carried out advantageously, therefore, it is desirable to enhance the efficiency of the activation by selecting the surface temperature of the film from the range between 15°C as the lower limit and the highest temperature at which no conspicuous shrinkage is caused in the film (80°C, for example).

As to the electrode, when rotary electrodes (roller electrodes) are used, the type of the electrode is not specifically limited. There may be used either a friction roll method or a drive roll method. The surface of the electrode is allowed to expose the metal or to be covered with rubber and the like, but it is necessary to give attention not to damage the film surface.

The electric discharge which is caused between the opposed inner surfaces of the film by the process of this invention is generally referred to as corona discharge or glow discharge. Even when this phenomenon of electric discharge is so feeble as to substantially escape observation by the naked eye, it is nevertheless found to impart active power to the film.

For the high-voltage flow of electric current required for the treatment of this invention, sufficient activation can be advantageously performed generally by using electricity ranging from 2.5 to 10 KV in potential and from 30 to 120 kilocycles in frequency, with the discharge time fixed in the range of from 0.05 to 0.2 second.

In this case, the film assumes improved printability and adhesiveness when the active power imparted in the film interior reaches a point where the meat-adhesiveness as determined by use of the mixture of albumin and starch falls in the range of from 0.5 to 1.0 mg/cm² and the haze similarly determined falls in the range of from 40 to 70%. For the film to assume the meat-adhesiveness in its outer surface, the activation is desired to be effected so much that the amount of the mixture adhered to the film surface is not less than 1.1 mg/cm² and the haze not less than 75%. For higher meat-adhesiveness, the activation is desired to be effected to a further extent such that the amount of the mixture adhered to the film surface exceeds 1.4 mg/cm² and the haze to exceed 80%.

Since the active power thus imparted to the film is considered to tend to decrease slightly with the lapse of time, it is desirable to give to the film as high active power as possible by taking into consideration such loss of the active power. The experiments conducted by the inventors have shown that no conspicuous loss of the active power occurs after the film is left to stand at 30°C for one month.

The devices illustrated in Fig. 6 and Fig. 7 fail to impart to the inner surface of the tubular film the active power of the level claimed to be desirable for the purpose of this invention.

The phenomenon of electric discharge which is observed in the treatment of this invention occurs without reference to the kind of synthetic resin used in the film and the condition of drawing of film (oriented or unoriented). When the electric-discharge treatment is performed on the film in a oriented form, the active power imparted thereby to the film is several times that imparted when this treatment is performed on an unoriented film and the treated film is subsequently oriented.

When the process of the present invention is applied to the process of continuous manufacture of what is called a seamless tubular film as by installing the device of Fig. 5 between the operation of orienting and that of winding or by feeding the tubular film (seamless or welded) out of the wound roll into the device of Fig. 4, there is derived an outstanding, heretofore unforeseeable advantage that the meat-adhesiveness can be imparted selectively to the inner surface of the tubular film in its original form.

The activation involved in the present invention, as already touched upon, has no direct bearing upon the oxidation of film surface or the coarsening of the film surface and has absolutely no possibility of giving rise to any poisonous substance. When this process is applied to the process for the manufacture of a film of vinylidene chloride resin which possesses properties befitting foodstuff packaging and which, because of delicate film-forming conditions, defies successful adoption of the conventional activating treatment, the film assumes high meat-adhesiveness hardly attainable by the prior art without entailing any degradation in the gas barrier property and the transparency of the film and imparting any objectionable odor to the film.

Generally by the process of this invention, just one treatment given by one pair of electrodes is sufficiently effective for the purpose of the activation. When necessary, there may be installed two or more pairs of electrodes to give the film the treatment in a stepwise manner. Particularly when two pairs of electrodes are disposed perpendicularly to each other with the axis of travel of the tubular film as the center so as to flatten the tubular film both vertically and horizontally into a generally rectangular cross section, there is brought about an advantage that stripes of untreated surface which tend to occur owing to the folding of the film can be completely eliminated.

The activation of the present invention can be effected on the film without any trouble even when a slidant such as talc or clay is adhering to the surface (outer and/or inner) of the film. In this respect, the present invention enjoys another advantage that the activation of the inner surface of the tubular film can be carried out on the tubular film which is in a state pretreated to facilitate the opening of the folded film.

There is a further advantage that this activation confers upon the film the meat-adhesiveness stable to a wide range of qualitative variation of the meaty substance to be packed with the film.

The words "synthetic resin" as used in the present invention are meant as a generic term which embraces polyolefin resins represented by polypropylene resin, polyethylene resin, ethylene-vinyl acetate copolymer resin and ionomer resin; vinylidene chloride resins made of copolymers obtainable by the copolymerization of a major portion (not less than 65%) of vinylidene chloride with a minor portion (less than 35%) of other copolymerizable component and of copolymers obtainable by the copolymerization of the two components just mentioned with a few percent of another resin; and combinations of the resins mentioned above.

Now the method of rating, the method of measurement and the criteria for the rating as involved in the present invention will be described herein below.

1) Method for rating meat-adhesiveness and haze by use of mixture of aqueous solution of albumin and starch (described already in the text page 17 line 16 to page 19 line 26).

2) Determination of meat-adhesiveness.

a) Preparation of Meaty Substance

A specimen for the determination of meat-adhesiveness is prepared by kneading a varying composition of ingredients shown in the following table.

Composition / Ingredients	I parts	II parts	III parts
Ground meat of pollock	40	40	—
Tuna	25	25	—
Pork	—	—	50
Lard	5	10	30
Starch	10	10	11
Spice	0.5	0.5	0.5
Table salt	2.5	2.5	3
Ice water	20	20	12

b) Method of Test

From a long strip of seamless tubular film given as a sample, a total of 15 pieces about 200 mm in length are cut out. Each piece is tied at one end and filled with the meaty substance. In this case, the meaty substances of the compositions (I), (II) and (III) are contained each in a total of five pieces of tubular film. After each piece has been filled with the meaty substance tightly to preclude entry of air, the remaining open end of the piece is tied, giving rise to a cylindrical package. This package is heated in hot water at 90°C for 50 minutes and then cooled in cold water at 20°C for one hour. Subsequently, the package is immersed in hot water at 96°C for five seconds to shrink the film and eliminate wrinkles, producing a sausage pack. Then two circumferential cuts are inserted at a longitudinal interval of 50 mm at a randonly selected position around the middle of the entire length of the cylinder and a longitudinal cut is inserted across the zone enclosed with the two circumferential cuts. A piece of film 50 mm in width is ripped off the circumference of the cylinder. From this piece of film, a square specimen 50 mm×50 mm is cut off.

c) Determination of Meat-Adhesiveness and Rating

The test pieces, n=5, obtained with respect to the three compositions (I), (II) and (III) are placed on a glass plate having squares drawn after the manner of checkerboard to find in the areas in which the meaty substances are adhering to the films. The proportion of the area thus found on each square piece to the total area of the square piece is found in percentage. Then, the values found for n=5 are averaged.

d) Criterion for Rating the Meat-Adhesiveness

⊙: more than 90% up to 100% (Excellent preservability of meaty substance)
○: more than 80% up to 90% (Good preservability of meaty substance)
Δ: more than 70% up to 80% (Deficient preservability of meaty substance)
x: more than 5% up to 70% } (Absence of feasibility of
x: 0 up to 5% } film for meat packaging)

3) Rating of Loss of Gas Barrier Property

a) Preparation of Test Piece and Method of Determination

A tubular film given as a sample is cut open to obtain a sheet film as the test piece. This test piece is examined for permeability to oxygen by the method specified by ASTM D-1434 (with a tester made by Mocon under conditions of 30°C±1°C and RH 90%) to find the value of permeability.

Separately, a standard sample (a film similar to the film under test in all respects with the only exception that it has not undergone the corona-discharge treatment) is tested in advance for the permeability to find the value. The rating of the loss of gas barrier property is made in terms of the difference between the value found for the test piece and the value found in advance for the standard sample (in cc/m². 2 hours . atm.).

b) Criterion for Rating

⊙: Up to 10 cc
○: More than 10 cc up to 30 cc
Δ: More than 30 cc up to 50 cc
x: More than 50 cc

4) Rating of Occurrence of Pinholes

a) Preparation of Test Piece and Method of Determination

From a given population of tubular films, a total of 200 tubular films 1 meter in length are randomly selected and each of them is tied at one end to assume the shape of a bag. Each bag of film is filled with compressed air and then tied at the other end, giving rise to a film cylinder filled with air. This cylinder is immersed under water. The presence or absence of a pinhole in the cylinder is determined by the presence or absence of air bubbles rising from the film surface. The number of pinholes in each cylinder is counted.

b) Criterion for Rating of Pinholes (Number of Pinholes/200 Tubular Films)

⊙: 0
O: 1 to 5
Δ: 6 to 10
x: 11 or over

5) Overall Rating

The overall rating is made on the following scale by taking into account the results of the rating of meat-adhesiveness (I), (II) and (III), those of the rating of loss of gas barrier property and those of the rating of occurrence of pinholes.

⊙: A combination of three double-circle marks "⊙" or a combination of two double-circle marks "⊙" plus one single-circle mark O"
O: A combination containing no cross mark "x" and only one triangle mark "Δ" plus two double circle marks "⊙" or a combination of two single-circle mark "O" and one double-circle mark "⊙"
Δ: A combination containing no cross mark "x" and two or more triangle marks "Δ"
x: A combination containing one or more cross marks "x"

6) Referential Rating

a) Rating of Surface Activation

The "wetting tension standard solutions" made by Wako Junyaku Kogyo (KK) are applied in the increasing order of dyne numbers to the surface of the film under test. The surface activation of the film is rated by the number of dynes of the standard solution which has retained intact the wetted area of the film surface for two seconds. In this case, the magnitude of surface activation increases with the increasing number of dynes.

b) Rating of Printability

b-1) The "printing ink for use with vinylidene chloride" make by Toyo Ink (KK) is applied with a hand coater to the surface of a film under test. The film is then left to stand at 20°C for 24 hours to allow the applied printing ink to set. After this standing, a cellophane tape available on the market is attached to the printed surface of the film and pressed hard to the film with finger tips. Then the cellophane tape is forcefully peeled off at an angle of about 30° relative to the surface of the film. The amount of the printing ink adhering to the cellophane tape (extent of separation from the film surface) is estimated by observation with the naked eye. The printability of the film is then rated by the scale, wherein:

	Marketability
⊙: Absolute absence of separation of printing ink	Excellent
O: Very slight separation of printing ink	Fair
Δ: Considerable Separation of printing ink	Passable
x: Heavy separation of printing ink	Not passable
✱: Complete separation of printing ink	Rejectable

b-2) The film containing the applied printing ink is crumpled between the fingers of both hands fifty times. Then it is spread out to examine the printed surface of the film and find any damage to the applied ink or separation of the applied ink by the scale, wherein:

Damage to applied ink	*Separation of applied ink*	*Marketability*
⊙: None	None	Excellent
O: Slight damage	None	Good
Δ: Appreciable damage	Slight separation	Passable
x: Appreciable damage	Appreciable separation	Not passable

c) Meat-Adhesive Power

In the skin of the cylindrical package filled with the meat (the meaty substance of the composition (I) used in the determination of meat-adhesiveness) and boiled, two longitudinal cuts are inserted at an

ment	Frequency (K.S.)	
tage (V)		
5	70	
5	70	
3	30	
2	80	
7	40	
7	50	
5	60	
5	60	
6	110	
5	60	
7	110	
—	1	

interval of 10 mm. The zone of the skin enclosed with the two cuts is pinched at the leading end. Then the leading end of the zone is lifted in such a manner as to peel the zone along the cuts. The tension generated in this case is measured by Tensilon (made by Toyo Seiki) in g/cm of width.

d) Amount of Meaty Substance Adhered to the Film Surface

The test piece cut from the cylinder-of-package in the determination of the meat-adhesive power is subjected to the weight-difference method to determine the amount of the meaty substance adhered to the test piece in terms of weight (mg) per cm^2 of area.

e) Rating of Exudation of Juice

The cylindrical package filled with the meaty substance and boiled is left to stand at 37°C for ten days. At the end of the standing, the package is undone and examined to determine whether or not there has occurred exudation of juice in the interface between the inner surface of the film and the surface of the packed mass of meaty substance by observation with the naked eye. In this case, occurrence of the exudation of juice is observed where the adhesion between the inner surface of the film and the surface of the packed mass of meaty substance is insufficient or when there is any uneven adhesion of meaty substance to the film surface. The film, when observed to suffer from exudation of juice, is rated low for its marketability.

Example 1 and Comparative Example 1

A vinylidene chloride copolymer of a varying composition shown in Table 1 (additionally containing about 7% of a plasticizer and a stabilizer) was fed to an ordinary melt extruder, melted and kneaded, then extruded in an annular shape, supercooled and drawn by the biaxial inflation method to produce a seamless tubular film 55 mm in design folded with and 0.04 mm in wall thickness.

A device for the corona-discharge treatment illustrated in Fig. 4 was installed between the step of orienting and the step of winding in the film-forming process described above. Under a varying set of conditions of corona-discharge treatment indicated in Table 1, the oriented seamless tubular film was treated to afford a tubular film.

The various tubular films obtained as described above were tested for adhesion of the albumin-starch mixture (amount of adhesion and haze of film due to adhesion), for meat-adhesiveness for the loss of gas barrier property and for the occurrence of pinholes and were rated respectively by the methods described above.

The results are collectively shown in Table 2.

In this case, Runs No. 1 through 6 represent preferred embodiments of this invention and Runs No. 7 through 12 represent comparative experiments. Run No. 12 represents an experiment wherein no electric-discharge treatment was given to the film.

The photographs of the inner surfaces of the tubular films of Runs No. 3 and No. 12 enlarged to 8,000 magnifications through a microscope are shown in Fig. 1 and Fig. 2 respectively.

Example 2

In 100 parts of a copolymer resin consisting of 80 parts of vinylidene chloride and 20 parts of vinyl chloride, 7 parts of dibutyl sebacate and 2 parts of epoxidized linseed oil were thoroughly dispersed. The resultant blend was fed to an extruder. By the ordinary melt inflation film-forming process used for the vinylidene chloride resin, it was drawn to produce a biaxially oriented seamless film 40 mm in flat width and 0.04 mm in wall thickness.

In this case, a device similar in construction to that which is illustrated in Fig. 4 was installed between the final roll and the winder shaft in the inflation step, to effect continuous manufacture of a seamless tubular film having the inner surface activated.

Main conditions involved in the activation treatment were 25 m/min of winding speed, 2 mm of space interposed between the inner surface of film, air as the gas sealed in the tube, iron-made rotary electrodes for electric-discharge treatment, 3 KV of applied voltage, 0.25 A of electric current for treatment, 100 Kc of frequency, one pair of electrodes and 30°C of film surface temperature. the [illegible] mixture and those of the referential rating are

Table 2

Results

of albumin-starch mixture								
Haze (%)	Amount adhered to film surface (mg/cm²)	Rating of Rating of meat-adhesiveness (II)	(III)	(IIII)	Rating of loss of gas barrier property	Rating of occurrence of pinholes	Overall rating
75	1.1	⊙	⊙	○	⊙	⊙	⊙
100	1.1	⊙	⊙	○	⊙	⊙	⊙
100	2.2	⊙	⊙	⊙	⊙	⊙	⊙
75	2.2	⊙	⊙	○	⊙	⊙	⊙
80	1.7	⊙	⊙	⊙	⊙	⊙	⊙
85	1.9	⊙	⊙	⊙	⊙	⊙	⊙
73	1.0	○	×	×	⊙	⊙	×
73	1.6	⊙	×	×	⊙	⊙	×
75	2.3	⊙	○	×	△	×	×
100	1.0	○	×	×	⊙	×	×
90	2.3	⊙	⊙	○	×	⊙	×
8	not more than 0.1	※	※	※	⊙	⊙	×

Table 3

	Example 2				*Comparative Example 2*				*Comparative Example 3*				*Comparative Example 4*				*Comparative Example 5*			
Test piece No. of film	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4
Amount of mixture adhered to film surface (mg/cm^2)	0.7	2.1	2.0	0.7	0.1	0.1	0.1	0.1	1.2	0.6	0.6	0.1	1.2	0.1	0.1	0.2	2.0	0.8	0.8	0.2
Haze (%)	60	92	90	60	8	8	8	8	75	60	60	10	75	10	10	20	90	60	60	20
Rating of surface activation (dyne)	39	44	44	39	34	34	34	34	41	37	37	41	41	34	34	37	44	39	39	35
Rating of printability (I)	Δ	◎	◎	Δ	×	×	×	×	○	×	×	×	○	×	×	×	◎	Δ	Δ	×
Rating of printability (II)	Δ	◎	◎	Δ	×	×	×	×	○	Δ	Δ	×	○	×	×	Δ	◎	Δ	Δ	×
Amount of meat adhered (mg/cm^2)	9.5				1				2.5				1.2				2.6			
Meat-adhesive power (g/cm of width)	40.5				0.3				3.0				0.3				3.5			
Occurrence of juice	No exudation				Exudation				Exudation				Exudation				Exudation			

In the table, the encircled numbers 1, 2, 3 and 4 serve to indicate front and rear surface of film: Encircled 1 and 4 designate outer surfaces and encircled 2 and 3 inner surfaces respectively.

Example 3

The procedure of Example 2 was repeated, except that air as the gas to fill the gap formed in the zone for inner surface treatment by electric discharge was changed to nitron gas, helium and argon respectively.

Comparative Example 6

The procedure of Comparative Example 3 was repeated, except that the air as the gas to fill the gap formed in the zone for inner surface treatment by electric discharge was changed to nitrogen gas, helium and argon. The results of Example 3 and those of Comparative Example 6 (rating by use of the albumin-starch mixture and referential rating) are collectively shown in Table 4.

Table 4

	Example 3						*Comparative Example 6*					
Gas sealed in the tube	*Nitrogen*		*Helium*		*Argon*		*Nitrogen*		*Helium*		*Argon*	
Test piece No. of film	2	3	2	3	2	3	2	3	2	3	2	3
Amount of mixture adhered to film surface (mg/cm^2)	1.7	1.8	1.9	2.0	1.6	1.6	0.6	0.7	0.7	0.7	0.6	0.6
Haze (%)	83	90	91	92	78	78	60	62	60	60	61	61
Rating of surface activation (dyne)	43	43	44	44	42	42	35	35	37	37	36	36
Amount of meat adhered (mg/cm^2)	9.1		9.5		8.9		2.3		2.5		2.4	
Meat-adhesive power (g/cm of width)	39.9		40.5		39.5		2.7		3.0		2.9	
Occurrence of juice	No exudation		No exudation		No exudation		exudation		exudation		exudation	

In the table, the encircled numbers 2 and 3 indicate inner surfaces of film.

Example 4

A seamless tubular film of low-density polyethylene 130 mm in flat width and 0.05 mm in wall thickness available on the market was pressed by two pairs of pinch rolls disposed at a distance from each other with air sealed inside the tubular film. The tubular film thus collapsed into a rectangular cross section was advanced longitudinally. A device of the construction shown in Fig. 5 was installed at a position around the middle of the aforementioned two pairs of pinch rolls to effect the treatment of the process of this invention on the tubular film in motion. Then the film was wound into a roll. In this treatment, the electric discharge was carried out between the inner surfaces of film at positions slightly deviating from the contact point of the pair of electrodes held in contact with each other via the film.

Main conditions of the treatment in this case were 30 m/min. of film winding speed, iron-made rotary electrodes for activation treatment, 5 KV of applied voltage, 0.2 A of electric current, one pair of electrodes, and 25°C of film surface temperature. The results of the rating of the film by use of the albumin-starch mixture and the referential rating are shown in Table 5.

Thereafter, the film was packed with meat and rated for meat-adhesiveness by following the procedure of Example 2.

Comparative Example 7

The procedure of Example 4 was repeated under the same conditions, except that the flow of electric current for electric discharge was stopped and the activation treatment was omitted. The results are collectively indicated in Table 5.

Table 5

	Example 4				*Comparative Example 7*			
Test piece No. of film	1	2	3	4	1	2	3	4
Amount of mixture adhered to film surface (mg/cm²)	less than 0.1	1.5	1.5 0.1	less than 0.1	less than 0.1	less than 0.1	less than 0.1	less than 0.1
Haze (%)	23	83	83	23	23	23	22	23
Rating of surface activation (dyne)	33	39	39	33	32	32	32	32
Amount of meat adhered (mg/cm²)	8.0				0			
Meat-adhesive power (g/cm of width)	32.5				0			
Occurrence of juice	No exudation				Exudation			

Example 5 and Comparative Example 8

Tubular films of vinylidene chloride-vinyl chloride copolymers possessing varying magnitudes of activation in the inner surfaces (charge ratio of VC1/VDC1=30/70, flat width 40 mm and thickness 0.04 mm) were suitably selected and they were tested for adhesive property and adhesive power by use of the albumin-starch mixture (by following the procedure of Example 2). The results are shown in Table 6.

Table 6

	Rating by use of albumin-starch mixture		*Meat-adhesive power (g/cm of width)*	*Marketability*
	Amount of adhesion (mg/cm²)	*Haze (%)*		
Example 5	1.1	76	8.1	Acceptable
	1.3	78	24.2	Best
	1.4	80	31.8	Best
	1.6	85	35.1	Best
	2.0	92	39.8	Best
Comparative Example 8	0.7	60	3.6	Rejectable

The present invention, by possessing the above mentioned structure, makes it possible to improve activity of the inner surface of the tubular film which could not be obtained by the conventional method. By this improvement, the step of turning inside out of the film can be omitted when printing on the inner surface of the film. Besides, the meat-adhesiveness can be given to the inner surface of the film by very simple process, and the film of less dispersion and having a large meat-adhesive power can be obtained continuously. Thus, this invention is excellent and has a high utility.

Example 6

A nylon, CM-1021 (made of (Toray) resin (1.202 of density and ordinary viscosity), a modified polyolefin resin (tradename "Admer VF500" made by Mitsui Petrochemical; specific gravity 0.930 and MFI 2.0), and a polyethylene resin (tradename "F-2135" made by Asahi-Dow, density 0.921 and MI 3.0) were fed to three different melt extruders. The resultant molten resins were joined in one T die to form a laminate composed of the three layers of polyethylene-Admer-nylon and extruded in the form of a sheet. The extruded sheet was subjected to roll drawing and tender drawing to afford a three-layer roll laminate 600 mm in width and 0.08 mm in wall thickness.

From the two rolls of this laminate, the films were unreeled, caused to advance through the device of Fig. 8, with the polyethylene layer sides thereof opposed to each other so as to under the activation treatment. The conditions of activation were 20 m/min of line speed, 2.5 mm of gap between the opposed films, 50 Kc of frequency and 6 KV of voltage. When the polyethylene resin sides of the films were subjected to the rating of Example 4, the results were equivalent to those of Example 4.

Owing to the construction described above, the present invention enables the tubular film to assume in the inner surface thereof the improved active power heretofore unattainable by the prior art. Consequently, for the purpose of printing on the inner surface of the tubular film, the step of turning the tubular film inside out can be omitted. This invention has an advantage that, by use of a very simple device, high meat-adhesiveness can be imparted quite uniformly to the inner surface of the tubular film continuously.

Thus, this invention is highly feasible.

Claims

1. A single- or multi-layered seamless tubular synthetic resin film, wherein when single-layered said tubular film is made of either an olefin resin or a vinylidene chloride resin containing substantially no functional group such as acid radical or acid amide radical and wherein when said tubular film is multi-layered the inner surface layer of said film is made of either an olefin resin or a vinylidene chloride resin containing substantially no functional group such as acid radical or acid amide radical, characterized in that the inner surface of said tubular film is activated to such an extent that the quantity of a mixture adhered to said inner surface ranges from 1.1 to 2.2 milligrams per square centimeter, said mixture consisting of albumin and starch and that the haze of said film to which the mixture adheres is not less than 75 percent, when said surface is treated with a mixture consisting of an aqueous albumin solution and starch.

2. The single- or multi-layered seamless tubular synthetic resin film according to claim 1, wherein the activity of the outer surface of the film is substantially nothing in contrast to the inner surface of the film.

3. The single- or multi-layered seamless tubular synthetic resin film according to claim 1 or 2, wherein the seamless tubular film is heat shrinkable.

4. A process for treating a tubular or flat synthetic resin film consisting of at least one layer with an electrode assembly comprising at least a pair of electrodes which are spaced and opposed to each other and which a high voltage current is applied to, characterized by activating inner film surface not in contact with said electrodes by means of conducting corona or glow discharge in the presence of a gas between inner film surfaces spaced and opposed to each other, while travelling said tubular film or flat film of double ply in the state of keeping the outer surface of said tubular film or the outer surface of each ply of said flat film in contact with said electrodes.

5. The process for treating a tubular or flat synthetic resin film according to claim 4, wherein the synthetic resin film is a seamless tubular film.

6. The process for treating a tubular or flat synthetic resin film according to claim 4, wherein the synthetic resin film is a flat film.

7. The process for treating a tubular or flat synthetic resin film according to claim 4, wherein the film surface layer to be activated is an olefin resin layer or a vinylidene chloride resin layer.

8. The process for treating a tubular or flat synthetic resin film according to claim 4, wherein the synthetic resin film is substantially oriented tubular film.

9. The process for treating a tubular or flat synthetic resin film according to claim 4, wherein the gap between the inner surfaces opposed to each other is not more than 5 millimeters.

10. A tubular or flat synthetic resin film consisting of at least one layer, having an activated inner surface or either surface activated, obtained in accordance with a process for treating said film with an electrode assembly comprising at least a pair of electrodes which are spaced and opposed to each

other and which a high voltage current is applied to, characterized by means of conducting corona or glow discharge in the presence of a gas between inner film surfaces spaced and opposed to each other, while travelling said tubular film or flat film of double ply in the state of keeping the outer surface of said tubular film or the outer surface of each ply of said flat film in contact with said electrodes.

11. The tubular or flat synthetic resin film consisting of at least one layer according to claim 10, wherein the synthetic resin film is a seamless tubular film.

12. The tubular or flat synthetic resin film consisting of at least one layer according to claim 10, wherein the synthetic resin film is a flat film.

13. The tubular or flat synthetic resin film consisting of at least one layer according to claim 10, wherein the film surface layer to be activated is an olefin resin layer or a vinylidene chloride resin layer.

14. The tubular or flat synthetic resin film consisting of at least one layer according to claim 10, wherein the synthetic resin film is substantially oriented tubular film.

15. The tubular or flat synthetic resin film consisting of at least one layer according to claim 10, wherein the gap between the inner surfaces opposed to each other is not more than 5 millimeters.

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